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## PARAFFIN HYDROCARBONS ISOLATED FROM CRUDE SYNTHETIC ISOOCTANE (2,2,4-TRIMETHYLPENTANE)

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### ABSTRACT

In connection with a study of the impurities present in the isooctane (2,2,4-trimethylpentane) certified for use as a primary standard reference fuel for the knock testing of motor fuels, a number of isoparaffin hydrocarbons have been obtained in a state of relatively high purity. The physical properties of these preparations which have been accurately measured include in most cases the freezing point, ASTM octane number, boiling point, refractive index, and density, the coefficients of variation of the last two with temperature, and the coefficient of variation of boiling point with pressure.

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## I. ORIGIN AND SCOPE OF INVESTIGATION

Normal heptane and the isooctane (2,2,4-trimethylpentane) are the compounds which have been adopted internationally as the primary standard reference fuels for the knock rating of automotive-engine fuels. In the latter part of 1934, the Cooperative Fuel Research Steering Committee, through its Subcommittee on Methods of Measuring Detonation,<sup>1</sup> requested the National Bureau of Standards to make an investigation of the impurities in these primary standards, with a view to developing specifications for purity.

As these materials are used for knock rating, it was necessary to determine not only the amount of each impurity present, but also its knock rating, as the total contamination which can be tolerated depends on the antiknock values of the constituents. Relatively large amounts of material had to be obtained in a state of reasonably high purity, as a knock rating requires a sample of about 200 ml. Smaller amounts of material of higher purity were obtained where possible and several physical properties of the purest materials were measured. In several instances preparations were obtained which appeared to be of higher purity than those heretofore described.

<sup>1</sup> Now the CFR Motor Fuels Committee.

## II. SOURCE MATERIALS

As certified isooctane has averaged about 99 percent pure, it is obvious that a very large amount of material would have to be processed in order to obtain the required amount of each impurity. However, the final purification of crude isooctane is by distillation, and the Röhm & Haas Co., manufacturers of isooctane, had on hand a quantity of forerun and still residue from this operation. They kindly offered to supply the quantity of each material required for this work. A total

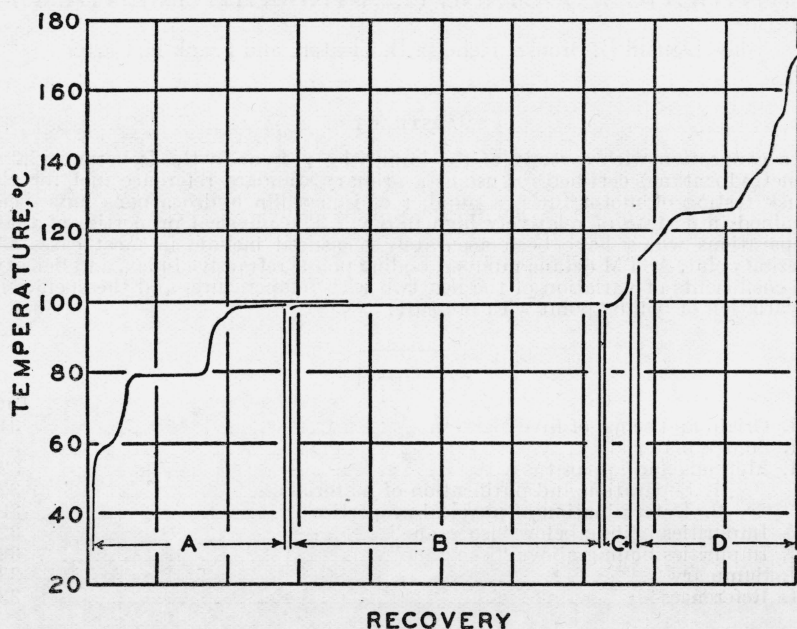


FIGURE 1.—Composite of fractional distillation of isooctane, forerun, and residue.

Portion A is the forerun from the purification of crude isooctane, B is a distillation of a sample of certified "isooctane", C is the distillation, in a small still, of the residue from B, and D is the still residue from the purification of crude isooctane.

of 6 gallons of forerun and a like amount of still residue were obtained from them. This represents the material rejected from over 300 gallons of crude isooctane.

A general picture of the materials involved is given in figure 1. In this figure the portion A represents data obtained in the first fractional distillation of the Röhm & Haas forerun. Portion B was obtained from a fractional distillation of a sample of batch 12 certified "isooctane", and C represents the distillation, in a small still, of the residue from B. Portion D shows data obtained in the first fractional distillation of the Röhm & Haas residue. The chart is arranged to show the relations between the boiling ranges of the three materials. The scales of recovery for the forerun and the still residue are magnified relative to that for the certified isooctane, the forerun being actually 1.25 percent, and the still residue 2.16 percent, of the crude isooctane. The principal impurities cause the flat portions at 79 and 125° C.

## III. METHODS AND APPARATUS

## 1. SEPARATION AND PURIFICATION OF MATERIALS

The forerun material was systematically distilled in 2.5-liter lots through fractionating columns packed with locket chain and having an efficiency of about 60 theoretical plates. The distillate was cut into portions boiling as follows: below 78° C, 78 to 81° C, 81 to 99.1° C, 99.2° C, and over 99.2° C. Similar fractions from successive lots were combined. When the entire supply of forerun had been so processed, each portion was again fractionated. Redistillation of each portion resulted in rejecting a certain amount of material to the next lower- and to the next higher-boiling portion, so that some further processing was required. In some cases, four successive fractionations were employed.

The still-residue material was first fractionated in a 30-plate bubble-cap column, and cut at 10° intervals up to 140° C, and at 20° intervals beyond 140° C. These cuts were then redistilled in locket-chain columns. For material normally boiling below 130° C the distillation was carried out at atmospheric pressure, while for that normally boiling above 130° C it was carried out at 215 mm Hg pressure.

In the further treatment of fractions, distillation was used when the quantity available was over 600 ml, and fractional crystallization by equilibrium melting [1],<sup>2</sup> or crystallization from methane when the quantity was less. Crystallization from methane by the method developed by R. T. Leslie [2] was found to be decidedly superior to fractional crystallization without solvent, although, in some cases, it was inferior to distillation where sufficient material was available to make the latter possible.

## 2. DETERMINATION OF PHYSICAL PROPERTIES

Freezing points of samples were determined by means of apparatus described elsewhere [3]. A platinum resistance thermometer, frequently calibrated, was used for temperature measurement. Reproducibility of freezing points was ordinarily about 0.03° C for materials of medium purity.

Boiling points of samples of low purity were measured in a Cottrell boiling-point apparatus, using mercury-in-glass thermometers which were calibrated frequently. Samples of higher purity were distilled through a 10-inch jacketed column [4], the jacket being heated electrically to a temperature such that slight condensation occurred in the column. This temperature was from 3 to 6° C below the boiling point of the sample. A platinum-resistance thermometer inserted in the column was used for the boiling-point measurement. The barometer used for air-pressure measurement was a Fuess Standard, graduated to 0.01 mm. Reproducibility of results, when corrected to 760 mm Hg, was about 0.01° C. All tabulated data given herein have been corrected to 760 mm Hg pressure.

Refractive indices of samples were measured on an Abbe refractometer (Valentine) graduated to 0.0001. This instrument was calibrated whenever tests were made, by measuring the index for distilled water, and for a sample of octane the index of which had been determined on a spectrometer. Results given in the tables herein are at 20 and 25° C for the *D* line of sodium.

<sup>2</sup> Figures in brackets refer to the references listed at the end of this paper.

Densities of less pure samples were measured by weighing a known volume on an analytical balance. Samples of high purity were measured by a pycnometer. All densities given in the tables herein are at 20° C, and are expressed as grams per milliliter.

#### IV. IMPURITIES BOILING BELOW "ISOOCTANE"

The forerun received from Röhm & Haas was found to consist of approximately 2 percent of pentanes, 5 percent of hexanes, 20 percent of heptanes, 72 percent of 2,2,4-trimethylpentane, and 0.5 percent of the higher-boiling compounds.

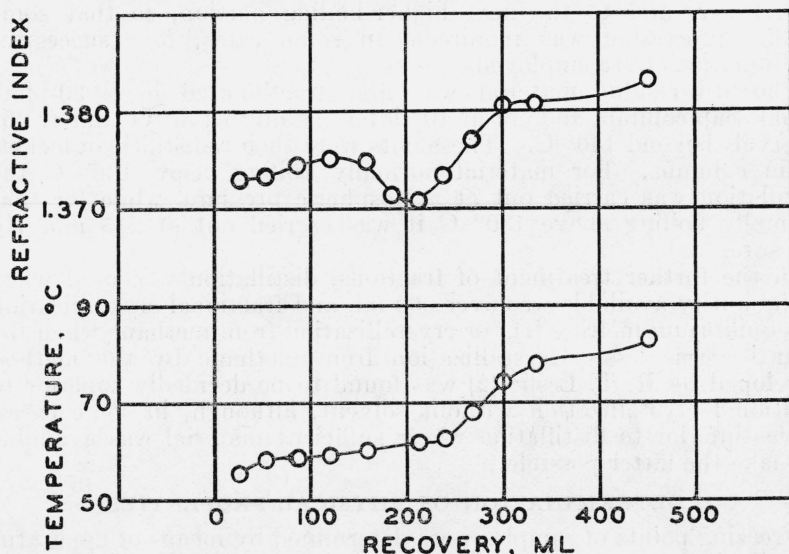


FIGURE 2.—Data obtained in fractional distillation of material originally fractionated below 78° C.

The boiling point of the first fraction of the distillation of the forerun, which varied from 48 to 55° C for different lots, suggests the presence of 2,2-dimethylbutane. The amount of this material recovered was not sufficient to make possible its positive identification.

A second fractionation of 1,100 ml of material fractionally distilling originally below 78° C yielded 450 ml of distillate. Data obtained on the fractions are shown in figure 2. Two hexanes were obtained from different portions of this material by fractional crystallization. The properties of these hexanes, designated as materials 1.12C and 1.13C, are given in table 1. The properties found in the literature for hexanes boiling in this range are also given in table 1 for comparison.

TABLE 1.—Properties of hexanes

Material	Boiling point, 760 mm Hg	Refractive index		Freezing point	ASTM octane number
		$n_D^{20}$	$n_D^{25}$		
1.12C.....	°C 59.1	1.3798	1.3774	°C -145.5	86.4
1.13C.....	61.8	1.3729	1.3706	-153.2	83.6
2,3-Me <sub>2</sub> Butane [6,14].....	58.02	1.3783	-----	-132.7	-----
2-MePentane [6,14].....	60.27	1.372	-----	-153.71	-----



A third successive fractional distillation of the portions of the forerun boiling between 78 and 81° C was made. The change of refractive index, boiling point, and freezing point throughout this distillation suggested the presence of a slightly higher-boiling compound in addition to the 2,2-dimethylpentane responsible for the flat at 79.2° C on the boiling-point curve. A fourth fractional distillation was made in a smaller still, charging the latter fractions and the still

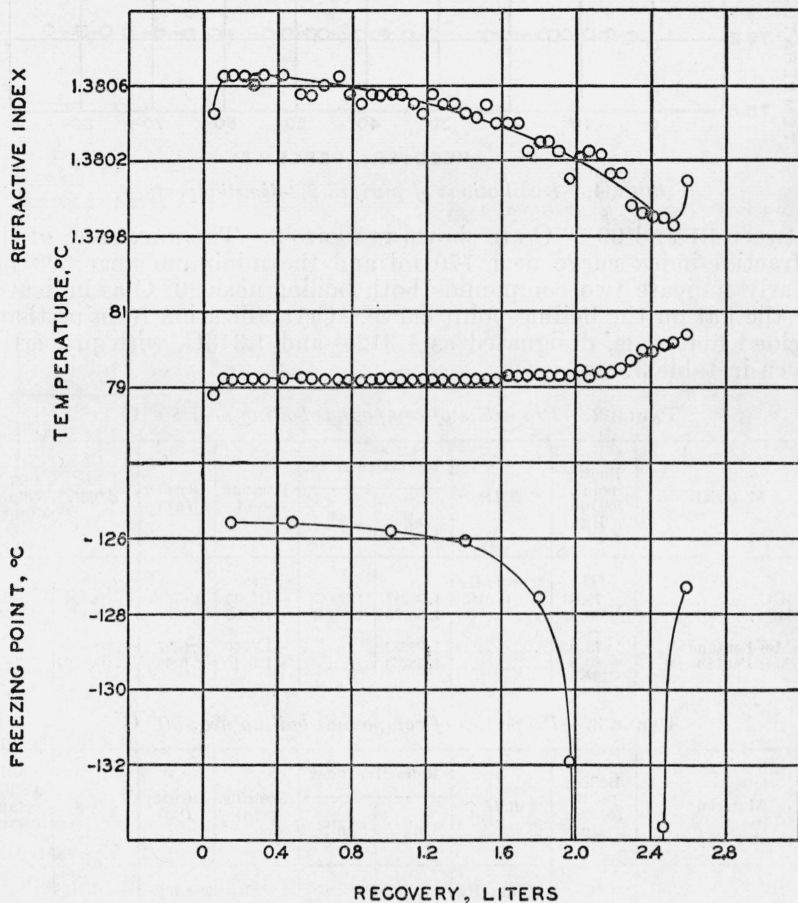


FIGURE 3.—Composite of fractional distillation of 2,2- and 2,4-dimethylpentane.

residue of the third distillation. The data obtained in this and the previous distillation have been combined and plotted in figure 3 and suggest the presence of 2,4-dimethylpentane. Two fractional crystallizations of the purer fractions of the less volatile material yielded a compound with a freezing point of 1.5° C below that found by Edgar and Calingaert [5] for synthetic 2,4-dimethylpentane. The properties of this material, designated as 1.2354CC, and of the purest 2,2-dimethylpentane, 1.233CC are given in table 2. The properties given by Edgar, Calingaert, and Marker for these compounds are also listed in table 2 for comparison. Distillation curves for the

purest samples of the two materials are shown in figures 4 and 5. Observations at two different values of atmospheric pressure have been corrected to 760 mm Hg pressure and are indicated by the two symbols in figure 4.

Data from the third fractionation of material originally boiling

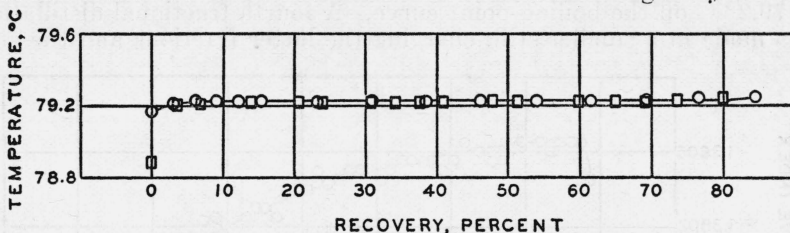


FIGURE 4.—Distillations of purified 2,2-dimethylpentane.

between 81 and 99.1° C are shown in figure 6. The maximum of the refractive-index curve near 170 ml and the minimum near 390 ml, clearly indicate two compounds both boiling near 90° C as indicated by the flat on the boiling-point curve. Crystallization from methane yielded materials, designated as 1.312C and 1.313C, with properties given in table 3.

TABLE 2.—Properties of compounds boiling near 80° C

Material	Boiling point, 760 mm Hg	$dt/dP$	Refractive index		Freezing point	Density $D/20$	$dD/dt$	ASTM octane number
			$n_D^{20}$	$n_D^{25}$				
1.233CC-----	°C 79.23	°C/mm Hg 0.0445	1.38247	1.38023	°C -125.43	g/ml 0.67513	g/ml/°C 0.000804	92.5
1.2354CC-----	80.41		1.38175	1.37949	-124.82			
2, 2-Me <sub>2</sub> Pentane [5]---	78.9	-----	1.38233	-----	-125.60	.6737	.000855	-----
2, 4-Me <sub>2</sub> Pentane [5]---	80.8	-----	1.38233	-----	-123.4	.6745	.000856	-----

TABLE 3.—Properties of compounds boiling near 90° C

Material	Boiling point, 760 mm Hg	$dt/dP$	Refractive index		Freezing point	Density $D/20$	$dD/dt$	ASTM octane number
			$n_D^{20}$	$n_D^{25}$				
1.312C-----	°C 89.50	°C/mm Hg 0.0487	1.3892	1.3868	°C -133.3	g/ml 0.6880	g/ml/°C 0.00092	84.5
1.313C-----	90.23		1.3882	1.3856	-134.3			
2, 3-Me <sub>2</sub> Pentane [5]---	89.7	-----	1.39201	-----	-----	.6952	.000848	-----
2-MeHexane [5]-----	90.0	-----	1.38509	-----	-119.10	.6789	.000855	-----

The properties found in the literature for hydrocarbons boiling near 90° C are given for comparison. Distillations of the purest samples of these materials are shown in figures 7 and 8.

In addition to the compounds described above, the Röhm & Haas forerun contained about 0.5 percent of material distilling above 99.2° C. A subsequent distillation of this material, the data of which are plotted in figure 9, indicates the presence in the forerun, and consequently in the product to a greater extent, of materials boiling as high as 136° C.

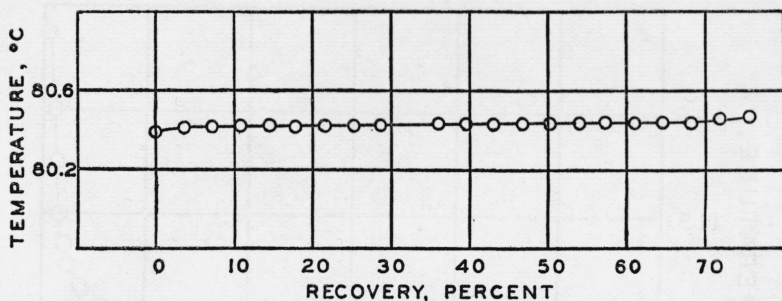


FIGURE 5.—Distillation of purified 2,4-dimethylpentane.

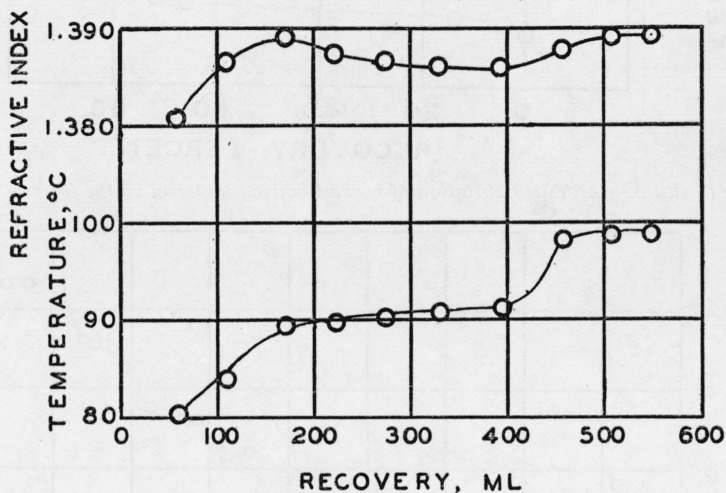


FIGURE 6.—Third fractional distillation of material boiling from 81 to 99.1° C.

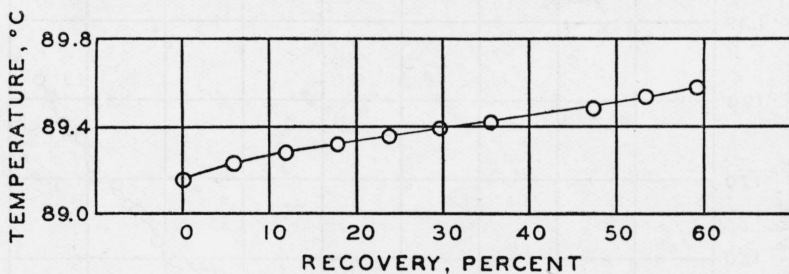


FIGURE 7.—Distillation of a purified heptane, probably 2,3-dimethylpentane.

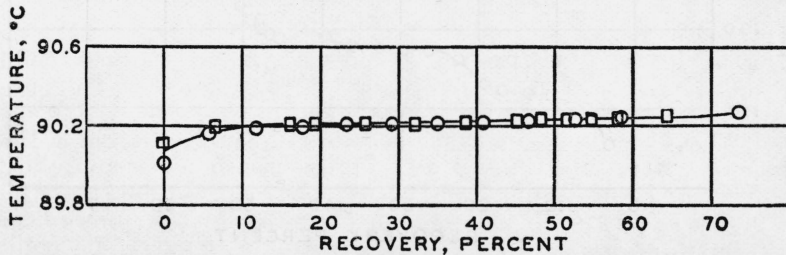


FIGURE 8.—Distillations of a purified heptane, probably 2-methylhexane.

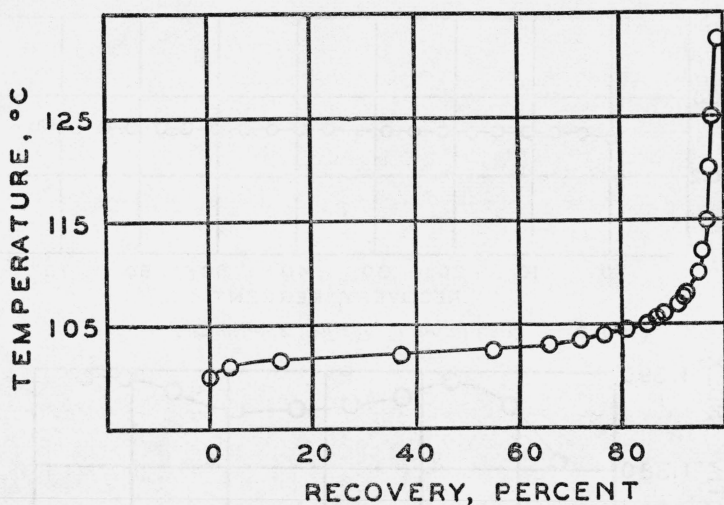


FIGURE 9.—ASTM distillation of highest-boiling material in the forerun.

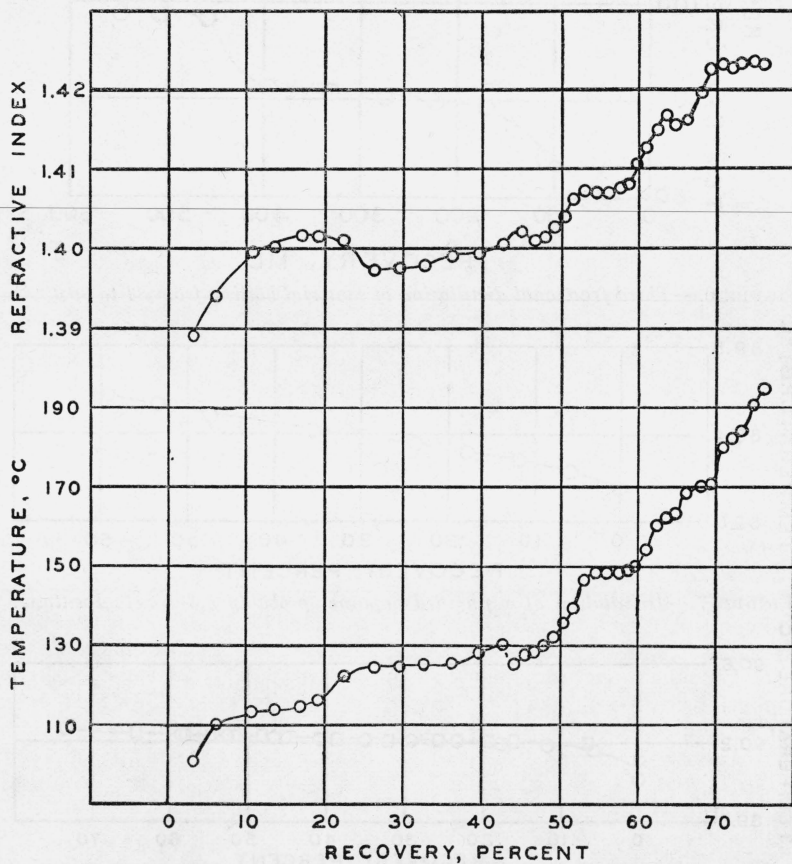


FIGURE 10.—Composite of fractional distillation of still residue from final distillation of crude isooctane.



The remainder of the forerun, about 72 percent, was 2,2,4-trimethylpentane. This material, purified by successive fractional distillations, yielded 2,2,4-trimethylpentane of high purity, which will be described in a subsequent paper.

## V. IMPURITIES BOILING ABOVE "ISOOCTANE"

Figure 10 gives a composite picture of the first fractional distillation of still-residue material. As mentioned earlier, distillation of material normally boiling above 130° C was actually carried out at 215 mm Hg pressure, to obviate cracking. Nearly one-fourth of the

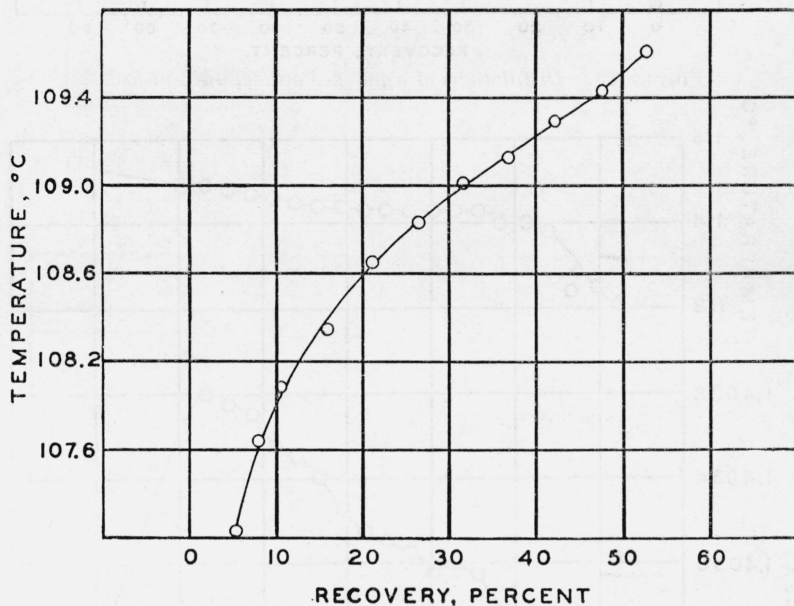


FIGURE 11.—Distillation of a purified octane, unidentified.

still residue did not distill at a temperature equivalent to 200° C at 1 atmosphere; no attempt has been made to investigate this part of the material. About 0.5 percent of the base stock distilled below 99.2° C; from its characteristics, it is believed to contain "isooctane" and octenes. Only about 1 percent of the Röhm & Haas residue was 2,2,4-trimethylpentane.

Fractional distillation of the material boiling between 100 and 110° C showed no other material boiling below 109° C. The material above 109° C was combined with the first material distilling from the 110 to 120° C cut, and again fractionally distilled. Properties of two portions of the resulting distillate, identified as 2.322CC and 2.323CC, which were twice crystallized from methane, are given in table 4 and the distillation curves of the purest samples of each are given in figures 11 and 12. Table 4 also gives the properties found in the literature for hydrocarbons boiling near 110° C.

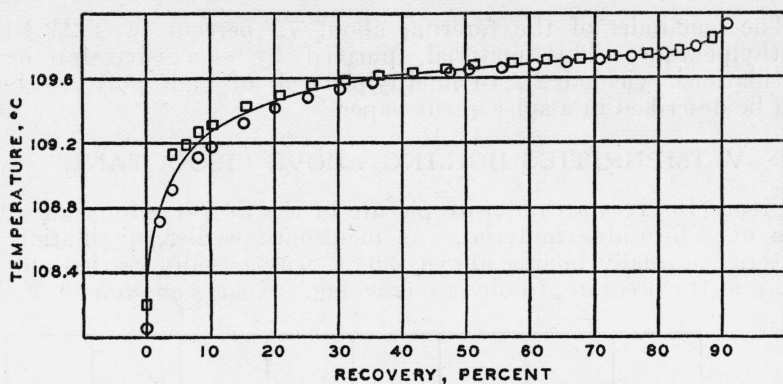


FIGURE 12.—Distillations of a purified octane, unidentified.

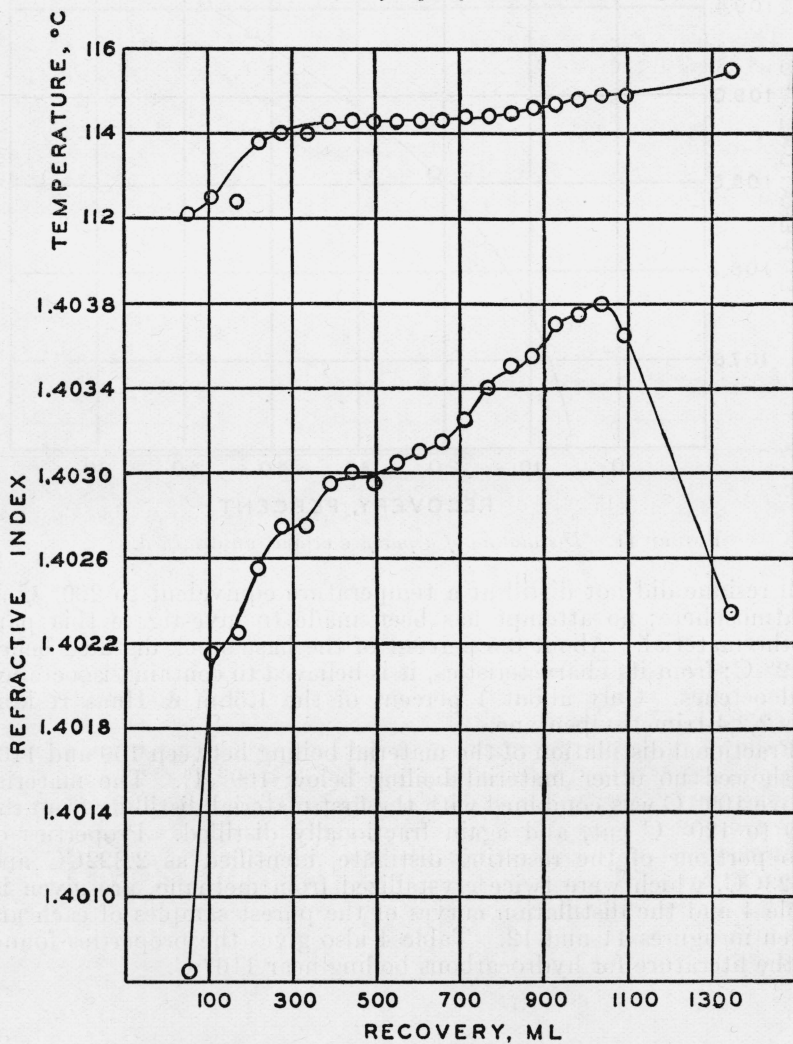


FIGURE 13.—Fourth fractional distillation of material boiling near 115° C.

TABLE 4.—Properties of compounds boiling near 110° C

Material	Boiling point, 760 mm Hg	$dt/dP$	Refractive index		Freezing point	Density $D_{20}$	$dD/dt$	ASTM octane number
			$n_D^{20}$	$n_D^{25}$				
	°C	°C/mm Hg			°C	g/ml	g/ml/°C	
2.322CC .....	109.5	-----	1.39926	1.39710	-125.0	0.7056	-----	94.8
2.323CC .....	109.65	0.0493	1.40069	1.39852	-122.4	.7108	0.00082	88.3
2,2-Me <sub>2</sub> Hexane [7] .....	106 to 107	-----	1.3931	-----	-----	.6967	-----	-----
2,4-Me <sub>2</sub> Hexane [6, 8] .....	{108.4 to 110}	-----	1.3950	-----	-----	{.698 to .700}	-----	-----
2,5-Me <sub>2</sub> Hexane [6, 7, 8, 9] .....	{107.5 to 109.2}	-----	{1.3922 to 1.3932}	-----	-91.3	{.693 to .698}	-----	-----
3,3-Me <sub>2</sub> Hexane [7] .....	111 to 112	-----	1.3998	-----	-----	.7116	-----	-----
2,2,3-Me <sub>3</sub> Pentane [6, 10] .....	{110.2 to 110.8}	-----	1.4030	-----	-----	.7173	-----	-----

The material in the next higher-boiling cut was subjected to successive fractionations, the last of which yielded data given in figure 13. The constant-boiling fractions were combined, as were the four fractions near the peak of the refractive-index curve. Two successive crystallizations from methane increased the diversity in characteristics of these two batches of material, proving the presence of at least two compounds. Properties of the final preparations designated as materials 2.3422CC and 2.3424CC, are given, with comparison data, in table 5, and their distillations are shown in figures 14 and 15.

TABLE 5.—Properties of compounds boiling near 114° C

Material	Boiling point, 760 mm Hg	$dt/dP$	Refractive index		Freezing point	Density $D_{20}$	$dD/dt$	ASTM octane number
			$n_D^{20}$	$n_D^{25}$				
	°C	°C/mm Hg			°C	g/ml	g/ml/°C	
2.3422CC .....	113.89	0.0484	1.40475	1.40263	-122.12	0.7200	0.00084	97.7
2.3424CC .....	114.64	-----	1.40661	1.40447	-114.83	.7249	.00089	99.1
2,3,4-Me <sub>3</sub> Pentane [10] .....	112.8	-----	1.4045	-----	-----	.7197	-----	-----
2,3,3-Me <sub>3</sub> Pentane [10] .....	113.6	-----	1.4074	-----	-----	.7258	-----	-----
2,3-Me <sub>2</sub> Hexane [6] .....	114	-----	1.4095	-----	-----	.719	-----	-----

Nearly one-fourth of the residue distilled between 120 and 130° C. Two fractional distillations separated this material into two compounds, one boiling at 124° C and one at 126° C. A third distillation of the 124° C material yielded fractions the freezing points of which are shown in figure 16. This material is characterized by an increasing propensity to subcool as its purity is increased. A freezing curve on the purest fraction is shown in figure 17. The 126° C material was twice crystallized from methane. Properties of the purest preparations of these two materials, designated as 2.422 and 2.52CC, are given in table 6, together with the properties found in the literature for 2,2,5-trimethylhexane. Distillation curves of the two materials are given in figures 18 and 19.

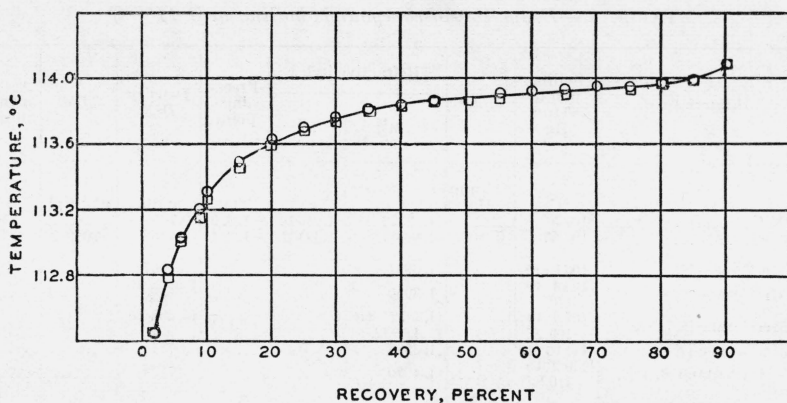


FIGURE 14.—Distillations of a purified octane, probably 2,3,4-trimethylpentane.

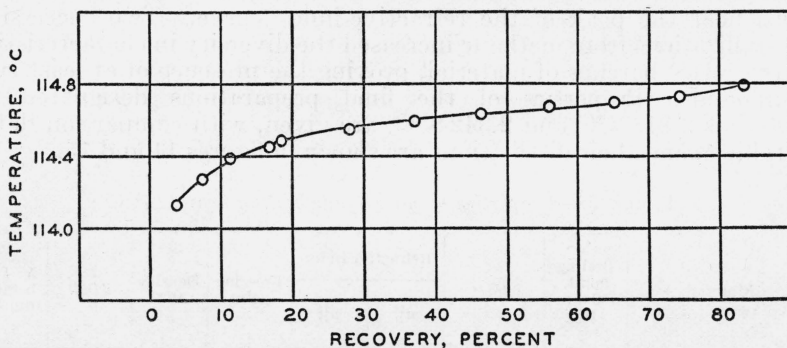


FIGURE 15.—Distillation of a purified octane, probably 2,3,3-trimethylpentane.

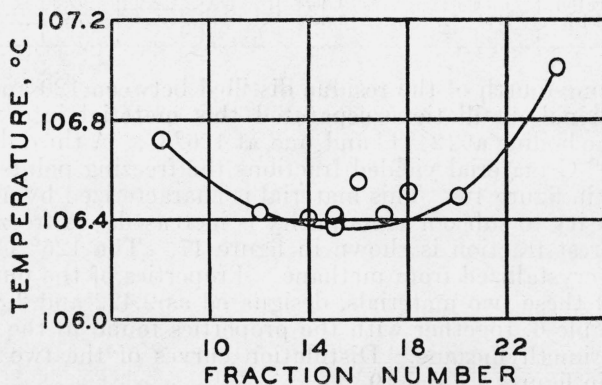


FIGURE 16.—Freezing points of fractions of purified 2,2,5-trimethylhexane.



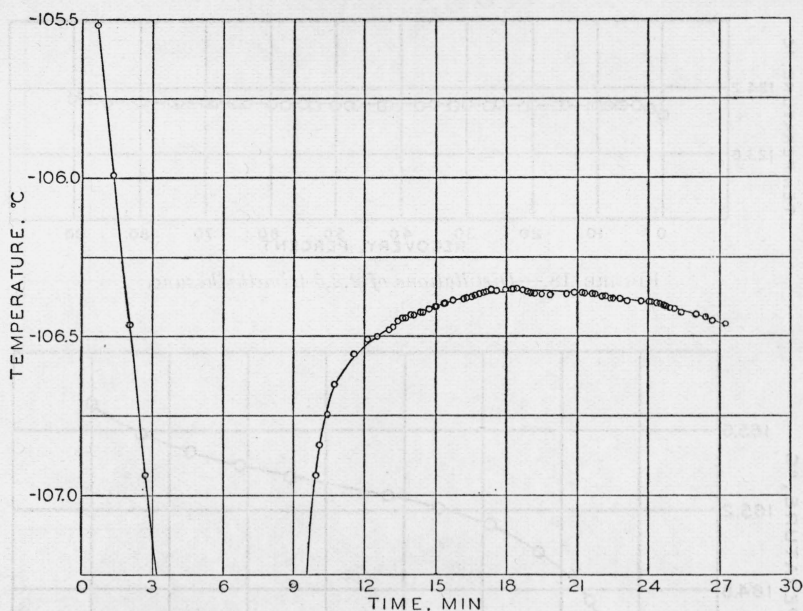


FIGURE 17.—Freezing curve of purest fraction of 2,2,5-trimethylhexane.

TABLE 6.—Properties of compounds boiling near 125° C

Material	Boiling point, 760 mm Hg	$dt/dP$	Refractive index		Freezing point	Density $D_{20}$	$dD/dt$	ASTM Octane number
			$n_D^{20}$	$n_D^{25}$				
2.422.....	°C 124.09	°C/mm Hg 0.0492	1.39967	1.39736	°C -106.35	g/ml 0.70755	g/ml/°C 0.000805	91.2
2.52CC.....	126.51	.0491	1.40312	1.40097	-129.53	.7048	.00083	92.1
2,2,5-Me <sub>3</sub> Hexane [7, 11].	{ <sup>121 to 123</sup> 126 }	-----	1.3997	-----	-----	.70911	-----	-----

A cryoscopic determination with benzene as the solvent gave 128.0 for the molecular weight of the 2.422 material. By analogy with properties given in the literature for 2,2,3-trimethylbutane, 2,2,4-trimethylpentane, and 2,2,6-trimethylheptane, it is clear that material 2.422 is 2,2,5-trimethylhexane, although the data given in the literature for the latter compound apparently were obtained on preparations of low purity. The 2.52CC material is, in view of its boiling point and octane number, probably a trimethylhexane. This is supported by the close agreement of its physical properties with those of the 2.422 material. Of the trimethylhexanes it seems probable that the 2,2,4-isomer would have properties most like those found for the 2.52CC material.

Small amounts of materials boiling between 132 and 142° C were obtained from the Röhm & Haas residue. None of these materials could be purified sufficiently to obtain a freezing point, although two were crystallized once from methane. The measured properties of the 2.54C material, given in table 7, agree reasonably with those given for 2,3,5-trimethylhexane, but its octane number, 66.9, is so low that it seems more likely that it may be 2,4-dimethylheptane.

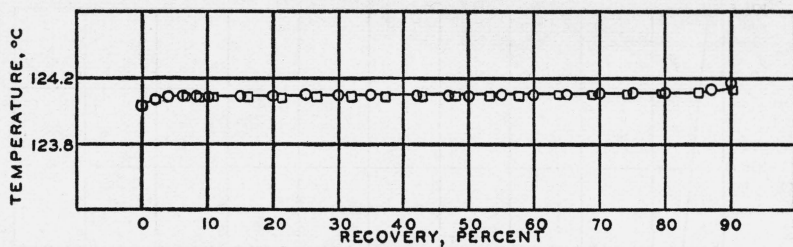


FIGURE 18.—Distillations of 2,2,5-trimethylhexane.

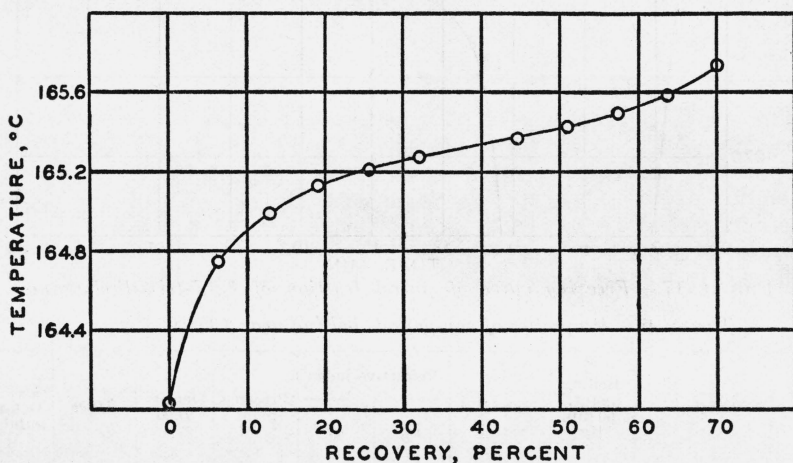


FIGURE 19.—Distillations of a purified nonane, probably a trimethylhexane.

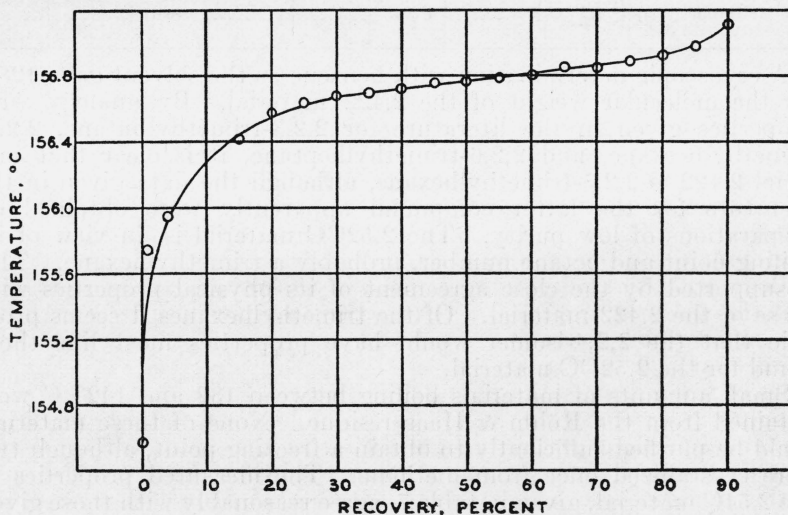


FIGURE 20.—Distillation of 2,2,6-trimethylheptane.

TABLE 7.—Properties of compounds boiling from 132 to 142° C

Material	Boiling point, 760 mm Hg	Refractive index		Density D/20	dD/dt	ASTM octane number
		$n_D^{20}$	$n_D^{25}$			
	° C			g/ml	g/ml/° C	
2.54C.....	132.1	-----	1.40305	0.7188	0.00088	66.9
2.62C.....	135.9	1.40664	1.40455	.7224	.00082	49.4
2.63.....	141.4	-----	1.4124	.738	-----	-----
2,3-Me <sub>2</sub> 3-EtPentane [12].....	141.60	1.4186	-----	-----	-----	-----
2,3,5-Me <sub>3</sub> Hexane [8].....	130	1.4051	-----	.716	-----	-----
2,3-Me <sub>2</sub> Heptane [12].....	140.6	1.4085	-----	.7235	-----	-----
2,4-Me <sub>2</sub> Heptane [7, 8].....	131 to 133	1.403	-----	.712 to .733	-----	-----
2,5-Me <sub>2</sub> Heptane [7, 8].....	133 to 137	1.4033	-----	.714	-----	-----
2,6-Me <sub>2</sub> Heptane [5, 6].....	132	1.401	-----	.707	-----	-----
3,3-Me <sub>2</sub> Heptane [7].....	137 to 138	1.4095	-----	.7304	-----	-----
4-EtHeptane [16].....	139	1.408	-----	.741	-----	-----

The physical properties of material 2.62C agree most nearly with those given for 3,3-dimethylheptane and the octane number lends support to this belief. Material 2.63 has properties close to those given for 4-ethylheptane; the small amount of 2.63 precluded any attempt to purify it further.

Material 2.65CC constituted about 6 percent of the Röhm & Haas residue. It was purified by twice crystallizing it from methane.

TABLE 8.—Properties of compounds boiling near 150° C

Material	Boiling point, 760 mm Hg	dt/dP	Refractive index		Freezing point	Density D/20	dD/dt	ASTM octane number
			$n_D^{20}$	$n_D^{25}$				
	° C	° C/mm Hg			° C	g/ml	g/ml/C	
2.65CC.....	148.93	0.0510	1.40777	1.40560	-105.0	0.7238	0.00087	78.7
2.68C.....	151.97	.0540	1.41278	1.41076	-----	.7349	-----	80.5
2.72C-1.....	156.77	-----	1.41353	1.41151	-----	.7374	.00081	53.2
2,2,6-Me <sub>3</sub> Heptane [11].....	151 to 152	-----	1.4090	-----	-----	.7215	-----	-----
2,4-Me <sub>2</sub> Octane [8].....	153.5	-----	1.4090	-----	-----	.725	-----	-----
2,6-Me <sub>2</sub> Octane [6].....	159 to 160.5	-----	1.411	-----	-----	.734	-----	-----

Comparing the properties of this material with the listed properties, table 8, of 2,2,6-trimethylheptane, and with additional properties extrapolated from those of the analogous isomers of fewer carbon atoms (sometimes referred to as the 2,2,2'-isomers), it seems certain that material 2.65CC is 2,2,6-trimethylheptane, although much purer than previous preparations. The distillation curve, figure 20, by analogy with those for similar materials of known purity, suggests that this material is about 98 percent pure.

A much small quantity of material 2.68C was recovered from the source material, and was crystallized from methane once. The properties of this preparation are given in table 8 and the distillation data in figure 21. No compound listed in the available literature shows similar properties. From the octane number it appears likely to be a trimethylheptane; the similarity between the respective properties of this material and 2,2,6-trimethylheptane, and of material 2.52CC and 2,2,5-trimethylhexane, suggests that 2.68C may be 2,2,4- or 2,2,5-trimethylheptane, although this is definitely speculative.

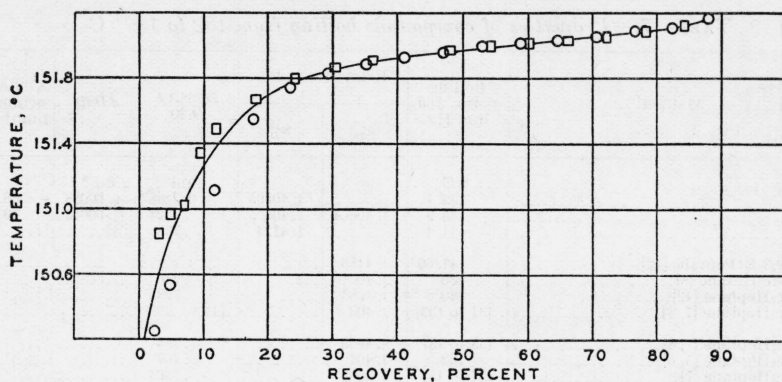


FIGURE 21.—Distillations of a purified decane, probably a trimethylheptane.

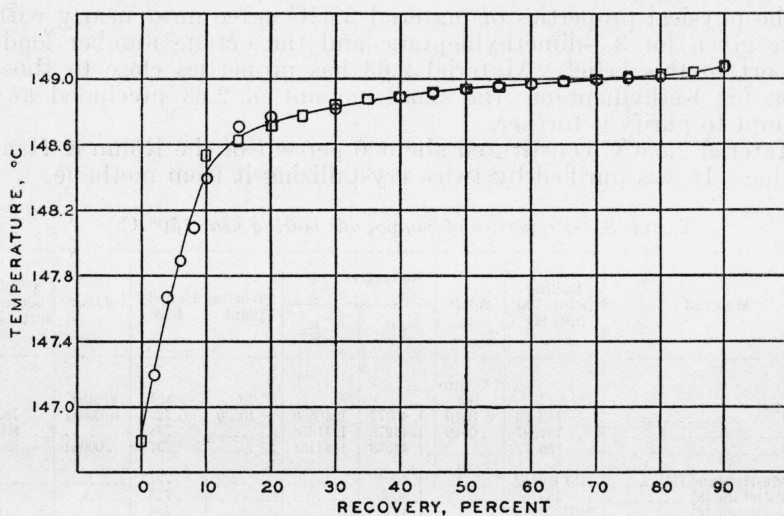


FIGURE 22.—Distillation of a purified decane, unidentified.

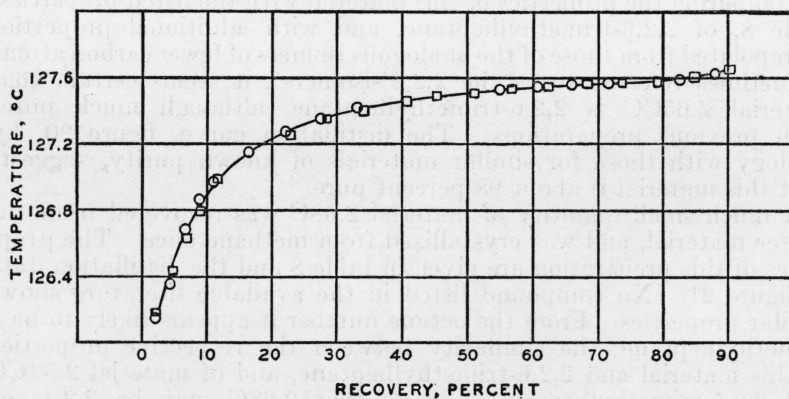


FIGURE 23.—Distillation of a purified decane, possibly 3,3,4,4-tetramethylhexane.



Material 2.72C-1, the properties of which are given also in table 8, and the distillation in figure 22, cannot be identified even tentatively, although its properties are close to those given for 2,6-dimethyloctane.

Materials 2.72C-2 and 2.74, the properties of which are given among those in table 9 and the distillation data in figures 23 and 24 are possibly the same material in different states of purity. These materials may be 3,3,4,4-tetramethylhexane.

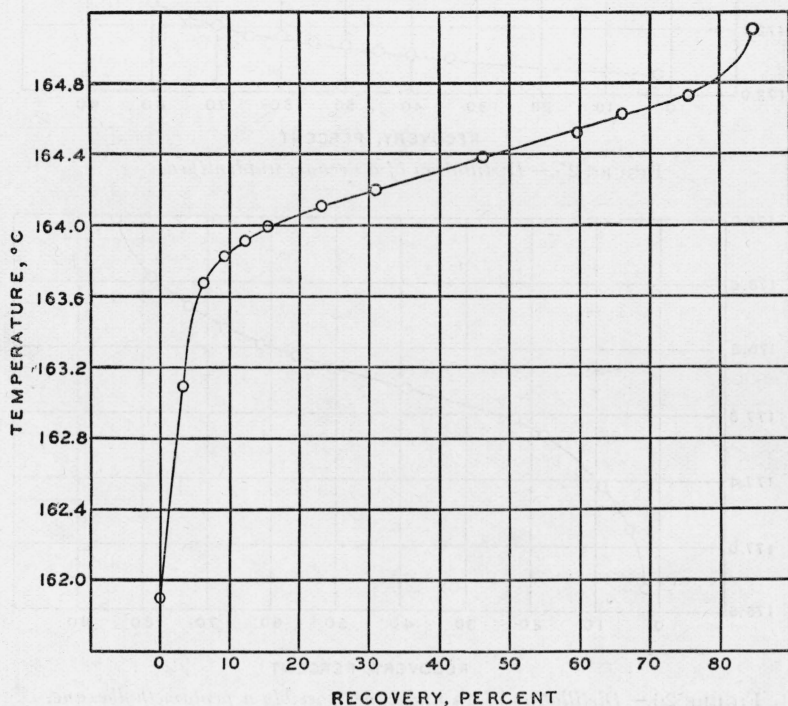


FIGURE 24.—Distillation of a purified decane, possibly 3,3,4,4-tetramethylhexane.

TABLE 9.—Properties of compounds boiling above 160° C

Materials	Boiling point, 760 mm Hg	Refractive index		Density $D_{20}$	$dD/dt$	ASTM octane number
		$n_D^{20}$	$n_D^{25}$			
	° C			g/ml	g/ml/° C	
2.72C-2 .....	165.42	1.42161	1.41956	0.7538	0.00081	69.2
2.74C .....	164.42	1.42229	1.42029	.7565	.00080	65.4
2.76 .....	172.28	1.4161	1.4138	.7430	.00070	68.4
2.78 .....	178.06	-----	1.4258	.7580	.00073	86.0
2.82C .....	182.76	1.42333	1.42130	.7539	.00074	78.4
3,3,4,4-Me <sub>4</sub> Hexane [13] .....	163.5	-----	-----	.7608	-----	-----
2,3,7-Me <sub>3</sub> Octane [8] .....	175	-----	-----	.756	-----	-----

The remaining materials listed in table 9 were obtained in small quantities, and, with the exception of 2.82C, would not crystallize from methane. Distillation curves for materials 2.76, 2.78, and 2.82C are given in figures 25, 26, and 27. These materials have not

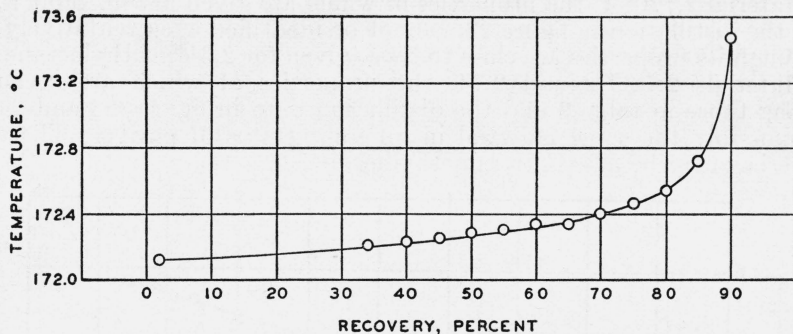


FIGURE 25.—Distillation of a decane, unidentified.

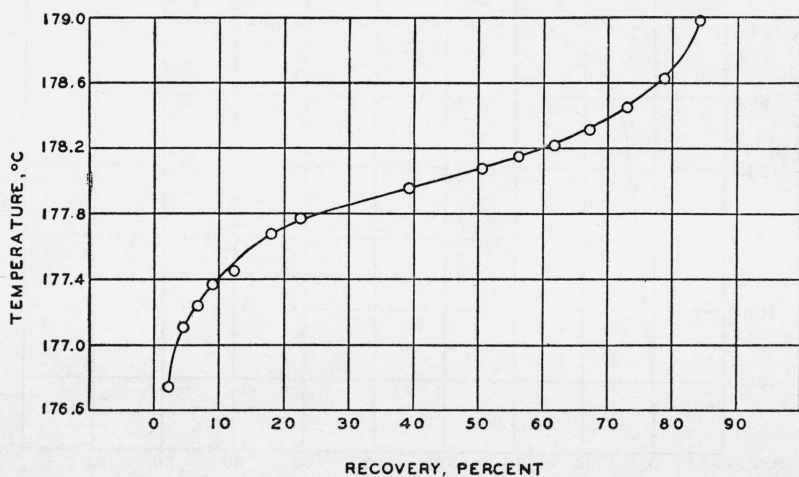


FIGURE 26.—Distillation of an undecane, possibly a pentamethylhexane.

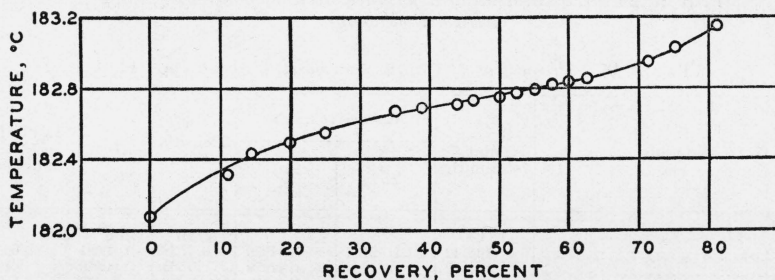


FIGURE 27.—Distillation of a purified undecane, unidentified.

been identified. Material 2.78, which from its boiling point must be an undecane, appears to have a highly branched chain, in view of its octane number. Its properties do not suggest the hexamethylpentane, but it is possibly one of the pentamethylhexanes, such as the 2,2,3,3,4-isomer. For a compound of so high a boiling point, this material has an unusually high octane number.

## VI. SUMMARY

In conclusion, the compounds listed in table 10 have been isolated from the crude synthetic isooctane, and have been identified with the degree of certainty indicated.

TABLE 10.—*Summary of compounds isolated*

Compound	Identification	Percentage present in crude
		<i>Percent</i>
2,2-Dimethylbutane.....	Probable.....	0.01
2,3-Dimethylbutane.....	Positive.....	.03
2-Methylpentane.....	do.....	.02
2,2-Dimethylpentane.....	do.....	.19
2,4-Dimethylpentane.....	do.....	.03
2,3-Dimethylpentane.....	Probable.....	.01
2-Methylhexane.....	do.....	.02
2,4-Dimethylhexane.....	} do.....	.04
2,5-Dimethylhexane.....		
3,3-Dimethylhexane.....	do.....	.04
2,3,4-Trimethylpentane.....	Positive.....	.12
2,3,3-Trimethylpentane.....	do.....	.10
2,2,5-Trimethylhexane.....	do.....	.50
2,2,4-Trimethylhexane.....	Probable.....	.10
2,4-Dimethylheptane.....	Doubtful.....	.03
3,3-Dimethylheptane.....	do.....	.04
4-Ethylheptane.....	do.....	.01
2,2,6-Trimethylheptane.....	Positive.....	.13
2,2,4- or 2,2,5-Trimethylheptane.....	Probable.....	.02
2,6-Dimethyloctane.....	Very doubtful.....	.02
3,3,4,4-Tetramethylhexane.....	Probable.....	.04
2,2,3,3,4-Pentamethylhexane.....	Very doubtful.....	.02

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